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⑭ 発明の名称 酸化チタンを含むポリエステル製造方法

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明 細 書

1. 発明の名称

酸化チタンを含むポリエステルの製造方法

2. 特許請求の範囲

テレフタル酸81を2N-KOH水溶液100mlに溶解して5mlのセルを用いて測定した340nmにおける吸光度が0.05-2.0であるテレフタル酸とエチレングリコールまたは該エチレングリコールとエチレンオキサイドを用い、リン化合物を添加して触媒の存在下に重縮合反応を行なわせ、反復精造単位の80%以上がエチレンテレフタレートからなるポリエステルを製造するに際し、重合段階以前において微粒子状のシリカおよび/またはアルミナと、酸化チタンとを添加することを特徴とする酸化チタンを含むポリエステルの製造方法。

3. 発明の詳細な説明

本発明は精製工程を省略した粗テレフタル酸を用いて反復精造単位の80%以上がエチレンテレフタレートから成る酸化チタン含有ポリエステルの製造するに際し、品質及び繊維製造時等の工

程性共に優れたポリエステルを得る方法に関するものである。

現在、工業的に繊維あるいはフィルムなどとして大量に使用されているポリエチレンテレフタレートはテレフタル酸ジメチル(以下DMTと略記する)とエチレングリコール(以下EGと略記)よりエステル交換反応およびこれに続く重縮合反応によつて製造されてきた。このエステル交換法は、テレフタル酸(以下TAと略記)を一旦メタノールと反応させてDMTとしたものをEGと反応させてメタノールを再び脱離させるという迂回した方法である。

これに対して、原料面でのコストダウンを目的としてDMTの代りにTAを用いて直接EGあるいはエチレンオキサイド(以下EOと略記)と反応させ、エステル化反応(EOとの付加反応をもエステル化反応と考える)および重縮合反応によつてポリエステルの製造する、いわゆる直接重合法(直重法)が次第に普及してきている。直重法で用いられるTAとしては、例えばP-ツアルキ-

SPECIFICATION

1. Title of the invention

Process for preparing polyester containing titanium oxide

2. Claims

A process for preparing polyester containing titanium oxide, which comprises using terephthalic acid having an absorbance of 0.06 to 3.0 at 340 m μ measured using a 5 cm cell by dissolving 8g of terephthalic acid in 100 ml of a 2N-KOH aqueous solution, and ethylene glycol, or the ethylene glycol and ethylene oxide, and adding a phosphorus compound to perform a polycondensation reaction in the presence of a catalyst, to prepare polyester comprising 80% or more of a repetition structural unit of ethylene terephthalate, wherein fine particulate silica and/or alumina, and titanium oxide are added before a polymerization stage.

3. Detailed Explanation of the invention

The present invention relates to a process of obtaining polyester excellent in both of quality and processibility at fiber manufacturing, upon preparation of titanium oxide-containing polyester comprising 80% or more of a repetition structural unit of ethylene terephthalate using crude

terephthalic acid undergoing no purification step.

Polyethylene terephthalate which is currently industrially used as a fiber or a film at a large scale has been prepared by a transesterification reaction from dimethyl terephthalate (hereinafter, abbreviated as DMT) and ethylene glycol (hereinafter, abbreviated as EG) and a subsequent polycondensation reaction. This transesterification method is a circumventing method of once reacting terephthalic acid (hereinafter abbreviated as TA) with methanol to obtain DMT, which is reacted with EG to leave methanol again.

To the contrary, for the purpose of reducing the cost of a raw material, a so-called direct polymerization method of using TA in place of DMT to react directly with EG or ethylene oxide (hereinafter, abbreviated as EO), and performing an esterification reaction (an addition reaction with EO is also regarded as an esterification reaction) and a polycondensation reaction has been gradually spread. As TA used in a direct polymerization method, for example, TA obtained by oxidizing p-dialkylbenzene with a molecular oxygen-containing gas, and further sufficiently purifying the resulting crude TA is used. As a method of purifying crude TA, a method of recrystallization from water or other solvent, and a method of performing oxidation or reduction treatment in a recrystallization process are performed. However, any of these methods need considerable steps, purification fee is high, and it is difficult to

sufficiently reduce polyester manufacturing cost.

Then, if crude TA can be used as it is in direct polymerization, considerable cost down is possible. However, under the present circumstances, when a polymer is prepared using crude TA, a tone of polyester is inferior, and a fiber having better whiteness can not be obtained as compared with purified TA. Recently, by improving the condition of oxidizing p-xylene, it has become possible to obtain crude TA having comparatively better quality. However, in such the case, since a production efficacy at TA manufacturing is inferior, sufficient cost down can not be attained and, as compared with the case where purified TA is used, the fiber whiteness is considerably inferior still. As the cause for a deteriorated tone of polyester when crude TA is used, coloring due to various impurities themselves contained in crude TA, or a coloring material produced by thermal degradation of impurities, or thermal degradation of a polyester main chain due to influence of the presence of impurities can be contemplated.

The present inventors previously studied extensively a process of obtaining polyester having a better tone using crude TA and, as a result, found that, by using crude TA having the specified optical property as a raw material, adding a specified phosphorus compound, and performing a polycondensation reaction in the presence of a catalyst of an antimony and/or germanium compound, polyester having remarkably improved

whiteness can be prepared.

However, when polyester is tried to be prepared using the aforementioned crude TA, and using titanium oxide as a matting agent in the presence of the phosphorus compound, titanium oxide is easily aggregated in a polymerization system, and the presence of the aggregate as a foreign matter in the polyester product is recognized. When such the foreign matter is present, for example, when a fiber is spun, clogging of a spinning filter and filament break at spinning are caused, it becomes difficult to perform spinning stably for a long term and, upon preparation of a film, reduction in the moldability and the mechanical property is recognized.

Therefore, an object of the present invention is to solve the aforementioned defects. The present inventors extensively studied a method of preventing titanium oxide from aggregating in the presence of a phosphorus compound using crude TA and, as a result, found that, by performing a polymerization reaction by adding fine particulate silica and/or alumina, the dispersity of titanium oxide is remarkably improved and, even when crude TA is used, the processibility at spinning is better, and polyester excellent in whiteness can be successfully prepared.

Although addition of fine particulate silica and/or alumina to a polyester synthesis reaction system is known, addition to a polymerization system using crude TA in the

presence of a phosphorus compound is not known. In addition, it is surprising that, even when those materials are added to a polymerization reaction system using DMT or purified TA, the dispersity of titanium oxide is not particularly improved, but the dispersity of titanium oxide is remarkably improved in a direct polymerization system using crude TA in the presence of phosphorus compound.

As the crude TA in the present invention, crude TA having an absorbance at 340 m μ (hereinafter, abbreviated as absorbance) of 0.06 to 3.0, preferably 0.08 to 2.5 measured using a 5 cm cell by dissolving 8g of TA in 100 ml of a 2N-KOH aqueous solution is used. When an absorbance is smaller than 0.06, whiteness is not improved even when a phosphorus compound is added. On the other hand, when an absorbance is 3.0 or larger, there is the effect of improving whiteness, but that effect is not great and, further, a whiteness level is low. Therefore, this can not be commercially used.

In addition, as TA in the present invention, crude TA obtained by oxidizing p-xylene using particularly a cobalt and/or manganese system catalyst and using lower fatty monocarboxylic acid such as acetic acid and propionic acid as a solvent by the method, for example, shown in JP-B No. 34-2666 gazette, JP-B No.35-4963 gazette, U.S.P. No. 3139452 specification and the like, is used.

When two or more TAs are used by mixing, it is enough that

an average of absorbances is within the range of the present invention.

As the phosphorus compound used in the present invention, a phosphorus compound containing one or more elements selected from C, H and O as a constituent element is used. A phosphorus compound containing other element has the insufficient effect of improving whiteness, and the reduced processibility, being not preferable.

As the phosphorus compound in the present invention, preferably, an oxo-acid compound of phosphorus such as phosphoric acid, phosphorous acid, hypophosphorous acid, phosphonic acid, phosphinic acid and a derivative thereof are used. Examples thereof include phosphoric acid, trimethyl phosphate, triethyl phosphate, tributyl phosphate, trioctyl phosphate, triphenyl phosphate, tricresyl phosphate, phosphorous acid, trimethyl phosphite, tributyl phosphite, trioctyl phosphite, triphenyl phosphite, tricresyl phosphite, hypophosphorous acid, phenylphosphonic acid, dimethyl phenylphosphonate, diphenyl phenylphosphonate, ethylphosphonic acid, diethyl ethylphosphonate, diphenylphosphinic acid, phenyl diphenylphosphinate and the like.

When an antimony compound is used as a catalyst, it is preferable to add a pentavalent phosphorus compound in order to prevent a deterioration of a tone due to antimony reduction.

However, a tri- or less-valent phosphorus compound can be used at a small amount. When a germanium compound is used as a catalyst, a phosphorus compound having an arbitrary atomic value is used.

An amount of a phosphorus compound to be added is arbitrary. In terms of an amount of a phosphorus atom (P: ppm) relative to a weight of a produced polymer, an amount in a range satisfying preferably:

$$50x + 3 \leq P \leq 800x + 1000 \quad (1)$$

(x represents an absorbance of crude TA)

more preferably:

$$80x + 6 \leq P \leq 500x + 600 \quad (2).$$

is used.

When an amount is smaller than the range of (1) equation, there is an extent of the effect of improving whiteness, but is not sufficient. In addition, even when the compound is added at an amount exceeding the range of (1) equation, the effect of improving whiteness is reduced and, conversely, the dispersity of titanium oxide is reduced, being not preerable.

In order that the effect of the present invention is exerted, a phosphorus compound is preferably added at a stage before $[\eta]$ (limiting viscosity obtained by dissolving a polymer in an equivalent weight mixed solution of phenol and tetrachloroethane, and measuring at 30°C; unit dl/g) of 0.30, at an initial stage of an esterification reaction, or a stage

where a majority of an esterification reaction is completed, and a polycondensation reaction is initiated. In particular, when a phosphorus compound is added at an initial stage of an esterification reaction, titanium oxide is remarkably aggregated. However, when particulate silica and/or alumina is (are) added according to the present invention, the dispersity of titanium oxide is considerably improved, and it becomes possible to add a phosphorus compound from a starting point of a reaction. This is effective for obtaining polyester having higher whiteness when crude TA is used, and is more preferable also from a viewpoint of operation.

An amount of titanium oxide to be added in the present invention is arbitrary depending on the desired product. A grade of a fiber will be described. In general, titanium oxide is added at an amount of 0.03 to 0.1% in the case of "bright", 0.3 to 0.6% in the case of "semidall", or 1.5 to 4% in the case of "fulldall", relative to a weight of the produced polyester.

Titanium oxide is added during a term from initiation of an esterification reaction to initiation of a polycondensation reaction under reduced pressure by the conventional method. In particular, according to the present invention, even when titanium oxide is added at an initial stage of an esterification reaction, the dispersity is very good.

In addition, as an agent for improving the dispersity of titanium oxide used in the present invention, fine particulate

silica and/or alumina is (are) used. A particle diameter is preferably a few micron (μ) or smaller, more preferably 0.1 μ or smaller. In the case of too large particle diameter, the effect of improving the dispersity is small, and such the particle becomes a foreign matter, and the spinning property is reduced, being not preferable.

When a material other than that in the present invention is added even in a fine particulate form, there is no effect. For example, even when ultrafine particulate titanium oxide is added together with normal titanium oxide, the dispersity is not improved at all.

An amount of fine particulate silica and/or alumina is not particularly limited, but usually, as an amount of a phosphorus compound and titanium oxide grows large, a more addition amount is required. In general, 0.001 to 4.0%, preferably 0.002 to 2.0% relative to a weight of the produced polyester is used. When an amount is smaller than 0.001%, the effect of improving the dispersity of titanium oxide is smaller. And, even when added at 4.0% or larger, the effect does not become considerably great.

Silica and/or alumina is added during a term from initiation of an esterification reaction to initiation of a polycondensation reaction under reduced pressure, in brief, until entrance into a final polymerization reaction, as in the case of titanium oxide. It is desirable to add silica and/or

alumina at the same time with or before addition of titanium oxide. However, when there is no great time lag, silica and/or alumina may be after addition of titanium oxide.

As fine particulate silica and/or alumina, various products are commercially available. A fine particle itself, or a dispersion of the fine particle in EG, or a colloid such as colloidal silica may be used.

As a polycondensation catalyst in the present invention, an antimony compound, a germanium compound, or a mixed system of an antimony compound and a germanium compound is used. Also, other catalyst system may be used and, in general, polyester having a better tone can not be obtained.

The polyester in the present invention is polyester composed of a repetition structural unit comprising 80% or more of ethylene terephthalate. And, isophthalic acid, phthalic acid, adipic acid, sebacic acid, propylene glycol, neopentyl glycol, tetramethylene glycol, 1,4-cyclohexanedimethanol, p-oxybenzoic acid, trimethylolpropane, pentaerythritol, glycerin, trimesic acid, methoxypolyethylene glycol, naphthoic acid, and sodium 3,5-dicarboxybenzenesulfonate may be copolymerized. In addition, polyester may contain a polymer such as polystyrene and polyethylene, or an additive such as an antioxidant, an optical brightening agent, a stabilizing agent and an ultraviolet absorbing agent.

When TA and EG are used as a main raw material, an

esterification reaction and a subsequent polycondensation reaction under reduced pressure are performed by the conventional method to obtain polyester. In addition, when TA and EO are used, a first step of preparing bis (β -hydroxyethyl) terephthalate (hereinafter, abbreviated as BHET) as a main product is performed, and the first step product is used as a starting material and, if necessary, TA is freshly added and, further, a polycondensation reaction is finally performed under reduced pressure to obtain polyester.

Then, the present invention will be specifically explained by way of Examples, but the present invention is not limited by them. In Examples, "part" representing an addition amount means a part by weight in all cases. In addition, the dispersity of titanium oxide is obtained by taking a polymer having $[\eta]$ of around 0.5, cut it into a thin piece, observing the piece with a microscope, and expressing as the number of coarse particles having a particle diameter of 10 μ or larger in 1 mm³. In addition, whiteness is a value obtained by extruding a polymer having $[\eta]$ of around 0.6 through a spinning die into a fiber, and measuring reflectances R_{450} and R_{550} of a polyester fiber at 450 m μ and 550 m μ with a tungsten light source using a spectrophotometer, from which the value is obtained using the equation: whiteness (unit; %) = $4R_{450} - 3R_{550}$. A greater numerical value indicates that whiteness is better.

The results of Examples are shown as a whole in Table 1.

Example 1

A polyester synthesis raw material containing 86 parts of TA having an absorbance of 0.6, 54 parts of EG, 0.5 part of titanium oxide, 0.03 part of antimony oxide as a polymerization catalyst, tributyl phosphite as a phosphorus compound at 0.05 part in terms of an amount of a phosphorus atom, and 0.1 part of Sonwtex O (aqueous dispersion colloidal silica having a particle diameter of 10 to 20 μ m; manufactured by Nissan Kagaku) as a dispersion improving agent was reacted at a temperature of 240°C and a pressure of 2.0 to 2.5 kg/cm² for 2 hours while removing the produced water, to perform an esterification (ES conversion) reaction. Then, the system was returned to a normal pressure, and a temperature was risen to 270°C for 30 minutes. Subsequently, a temperature was risen to 285°C for 30 minutes while the system was gradually evacuated (final pressure; 20 mmHg), and a pre-polymerization reaction was performed. Further, a polycondensation reaction was performed at 285°C under high vacuum of 1 mmHg or smaller until $[\eta]$ reached around 0.6. After polymerization, the polymer was extruded through a spinning die to obtain a fiber. During polymerization, at a stage of $[\eta]$ of around 0.5, a sample for determining the dispersity of titanium oxide was taken.

The number of coarse particles was 0/mm³, whiteness was 79% and, therefore, a fiber excellent both of the titanium oxide

dispersity and whiteness could be obtained using crude TA.

Comparative Example 1

According to the same manner as that of Example 1 except that Snowtex O was not added, a polymerization reaction and conversion into fiber were performed to obtain a polyester fiber having the number of coarse particles of $12/\text{mm}^3$ and whiteness of 77%. That is, whiteness was better, but the titanium oxide dispersity was worse.

Comparative Example 2

According to the same manner as that of Example 1 except that tributyl phosphite and Snowtex O were not added, a polymerization reaction was performed to obtain polyester having the number of coarse particles of $2/\text{mm}^3$ and whiteness of 48%. That is, the titanium oxide dispersity was considerably better, but whiteness was worse.

Comparative Example 3

According to the same manner as that of Example 1 except that tributyl phosphite was not added, a polymerization reaction was performed to obtain polyester having the number of coarse particles of $2/\text{mm}^3$ and whiteness of 49%. That is, the titanium oxide dispersity was not particularly improved as compared with Comparative Example 2, and whiteness was worse.

Comparative Example 4

According to the same manner as that of Comparative Example 2 except that purified TA (absorbance 0.04) was used, a polymerization reaction was performed to obtain polyester having the number of coarse particles of 1/mm³ and whiteness of 83%.

Comparative Example 5

According to the same manner as that of Comparative Example 4 except that Sonwtex O was added, a polymerization reaction was performed to obtain polyester having the number of coarse particles of 2/mm³ and whiteness of 82%. From Comparative Examples 4 and 5, it is seen that use of an agent for improving the dispersity is not preferable in the number of coarse particles and whiteness, in the case of purified TA.

Examples 2 to 7 and Comparative Examples 6 to 11

According to the same manner as that of Example 1, a polymerization reaction was performed by changing an absorbance of TA, a kind, an amount and an addition time of a phosphorus compound (after ES indicates after an ES conversion reaction), an amount of titanium oxide, a kind and an amount of an agent for improving dispersity, and a polymerization catalyst. Titanium oxide and an agent for improving dispersity

were added before ES reaction, respectively. As shown in Table 1, when an agent for improving dispersity was added, the dispersity was considerably improved in all cases.

Snowtex N is an aqueous dispersion colloidal silica having a particle diameter 10 to 20 μ manufactured by Nissan Kagaku, and an addition amount is expressed by pure silica. Aerosil 380 is fine particulate silica having a particle diameter of about 7 μ manufactured by Nippon Aerosil Co., Ltd., Cyloid 150 is fine particle silica having a particle diameter of 2.2 μ manufactured by Fuji Davison Ltd., and Aluminum Oxide C is fine particle aluminum oxide having a particle diameter of about 20 μ manufactured by Nippon Aerosil Co., Ltd.

Example 8

A mixture obtained by mixing 86 parts of TA having an absorbance of 0.6, 72 parts of EO and 1 part of triethylbenzylammonium chloride was reacted at 100 to 120 °C and 15 to 22 kg/cm² for 30 minutes to obtain the product, from which excessive EO was removed, recrystallized with water once and dried to obtain BHET. A polyester synthesis raw material containing 77 parts of this BHET, 36 parts of TA which was used as described above, 7.3 parts of EG, 0.5 part of titanium oxide, 0.012 part of germanium oxide, 0.05 part (in terms of an amount of a phosphorus atom) of tributyl phosphite and 0.1 part of Aerosil 200 (fine particulate silica, particle diameter about

12 μ , Nippon Aerosil) was esterified under pressure according to the same manner as that of Example 1 until water was hardly produced. Then, according to the same manner as that of Example 1, temperature rising, pre-polymerization and a final polymerization reaction were performed to obtain polyester having the number of coarse particles of 0/mm³ and whiteness of 82%.

Comparative Example 12

According to the same manner as that of Example 8 except that Aerosil 200 was not added, a polymerization reaction was performed to obtain polyester having the number of coarse particles of 11/mm³ and whiteness of 81%.

Example 9

According to the same conditions as those of Example 1 except for an amount of an agent for improving dispersity, polymerization was performed to further obtain a fiber. In this Example, an amount of an agent for improving dispersity is 0.01 part, the number of coarse particles is 0/mm³, and whiteness is 78% and, thus, a fiber excellent in both of the titanium oxide dispersity and whiteness could be obtained.

Example 10

According to the same conditions as those of Example 1

except that an amount of an agent for improving dispersity was 0.003 part, polymerization was performed to further obtain a fiber. The number of coarse particles is $1/\text{mm}^3$ indicating clear effect of an agent for dispersity, and whiteness is 79% and, thus, a fiber excellent in both of the titanium oxide dispersity and whiteness could be obtained using crude TA.

Comparative 13

According to the same manner as that of Example 1 except that 0.2 part of Titanium Oxide P25 (fine particulate titanium oxide, particle diameter about 30 μ , Nippon Aerosil Co., Ltd.) was added in place of Snowtex O, a polymerization reaction was performed to obtain polyester having the number of coarse particles of $15/\text{mm}^3$ and whiteness of 78%.

Table 1

No.	Glycol component	TA absorbance	Phosphorus compound			Titanium oxide (% by weight)	Dispersity improving dispersion		Polymerization catalyst		Number of coarse particles (/mm ³)	Whiteness (%)
			Kind	P atom ppm	Addition time		Kind	(% by weight)	Kind	ppm		
Example 1	EG	0.6	Tributyl phosphite	500	Before ES	0.5	Snowtex O	0.1	Antimony oxide	300	0	79
Comparative Example 1	EG	0.6	Tributyl phosphite	500	Before ES	0.5			Antimony oxide	300	12	77
Example 2	EG	0.6	-			0.5			Antimony oxide	300	2	48
Comparative Example 3	EG	0.6	-			0.5	Snowtex O	0.1	Antimony oxide	300	2	49
Comparative Example 4	EG	0.04	-			0.5			Antimony oxide	300	2	82
Comparative Example 5	EG	0.04	-			0.5	Snowtex O	0.1	Antimony oxide	300	2	82
Example 2	EG	0.1	Tributyl phosphite	30	Before ES	0.5	Snowtex O	0.02	Antimony oxide	300	0	82
Comparative Example 6	EG	0.1	Tributyl phosphite	30	Before ES	0.5			Antimony oxide	300	4	82
Example 3	EG	1.2	Phosphoric acid	500	Before ES	0.5	Snowtex O	1.5	Antimony oxide	300	2	74
Comparative Example 7	EG	1.2	Phosphoric acid	500	Before ES	0.5			Antimony oxide	300	19	73
Example 4	EG	0.6	Trioctyl phosphite	500	Before ES	2.0	Aerosil 380	0.5	Antimony oxide	300	2	78
Comparative Example 8	EG	0.6	Trioctyl phosphite	500	Before ES	2.0			Antimony oxide	300	15	77
Example 5	EG	0.6	Trioctyl phosphite	500	After ES	0.5	Cyloid 150	0.3	Antimony oxide	300	1	77
Comparative Example 9	EG	0.6	Trioctyl phosphite	500	After ES	0.5			Antimony oxide	300	4	77
Example 6	EG	0.3	Triethyl phosphite	300	Before ES	0.1	Aluminium Oxide C	0.3	Antimony oxide	300	1	81
Comparative Example 10	EG	0.3	Triethyl phosphite	300	Before ES	0.1			Antimony oxide	300	4	80
Example 7	EG	0.1	Phosphorous acid	30	Before ES	0.5	Snowtex N	0.05	Germanium oxide	120	0	85
Comparative Example 11	EG	0.1	Phosphorous acid	30	Before ES	0.5			Germanium oxide	120	5	84
Example 8	EO	0.6	Phosphorous	500	Before	0.5	Aerosil	0.1	Germanium oxide	120	0	82

Comparative Example 12	EO	0.6	acid Triethyl phosphite	500	ES Before ES	0.5	200	oxide Germanium oxide	120	11	81
Comparative Example 13	EG	0.6	Triethyl phosphite	500	Before ES	0.5	Titanium Oxide P25	Antimony oxide	300	15	78